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A study on the relationship between mass concentrations, chemistry and number size distribution of urban fine aerosols in Milan, Barcelona and London

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Abstract

A physicochemical characterization of the urban fine aerosol (aerosol number size distribution, chemical composition and mass concentrations) in Milan, Barcelona and London is presented in this article. The objective is to obtain a comprehensive picture on the involvement of the microphysical processes of the aerosol dynamic in the: 1) regular evolution of the urban aerosol (daily, weekly and seasonal basis) and in the day-to-day variations (from clean-air to pollution-events), and 2) link between "aerosol chemistry and mass concentrations" with the "number size distribution".

The mass concentrations of the fine PM2.5 aerosol exhibit a high correlation with the number concentration of particles >100 nm (which only accounts for <20% of the total number concentration N of fine aerosols) and do not correlate with the number of particles <100 nm ("ultrafine particles", which accounts for >80% of fine particles). Organic matter (OM) and black-carbon (BC) are the only aerosol components showing a significant correlation with ultrafine particles (attributed to vehicles emissions), whereas ammonium-nitrate, ammonium-sulphate and also OM and BC correlate with N>100(nm) (attributed to gas-to-particle transformation mechanisms and some primary emissions). Time series of the aerosol DpN diameter (dN/dlogD mode), mass PM2.5 concentrations and number N>100(nm) concentrations, exhibit correlated day-to-day variations which point to a significant involvement of condensation of semi-volatile compounds during urban pollution events. This agrees with the fact that ammonium-nitrate is the component exhibiting the highest increases from mid-to-high pollution episodes, when the highest DpN increases are observed. The results indicates that "fine PM2.5 particles urban pollution events" tend to occur when condensation processes have made particles grow enough to produce significant concentrations of N>100(nm). In contrast, because the low contribution of ultrafine particles to the fine aerosol mass concentrations, high "ultrafine particles N<100(nm) events" frequently occurs under low PM2.5 conditions. The data of this study point that vehicles emissions are strongly involved in this ultrafine particles aerosol pollution (for example,

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the “morning-rush-hours to nocturnal-background” concentrations ratio is 1.5–2.5 for “particles 10–100 nm” and <1.5 for both “particle >100 nm and PM2.5”).

1 Introduction

Atmospheric aerosol (or particulate matter-PM) is now one of the most concerning air pollutants owing to its ability to influence on climate, its adverse effects on human health and the difficulties in controlling their emissions (e.g. Wichmann et al., 2000; Sun et al., 2005; IPCC, 2001). Studies on urban fine atmospheric aerosol are experiencing a growing interest owing to: 1) the aerosol characterisation is difficult because it is made up of a complex mixture of solid and liquid substances (some of them semi-volatile) with a large range in particle size and 2) the still not very well characterised links between “urban and regional air quality” and “climate change”.

This concern on aerosol pollution in Europe has resulted in several studies focused on the composition and physical properties of PM throughout the continent (e.g. Ruuskanen et al., 2001; Van Dingenen et al., 2004; Putaud et al., 2004; Querol et al., 2004; Götschi et al., 2005; Rodríguez et al., 2007). In Europe, fine PM2.5 particles are mainly constituted by primary and secondary matter linked to combustion emissions, and also by mineral dust and sea salt. Although, the sources and composition of fine particles are being understood (except the biogenic contribution to organic matter; e.g. Janson et al., 2001), there are still significant uncertainties. The involvement of the different microphysical processes of the aerosol dynamics (i.e. nucleation, coagulation, condensation, evaporation, etc...) in the “urban and regional fine aerosol pollution events” has not deeply been characterized. In order to contribute to reduce the uncertainties on this subject, we have performed a study on fine aerosols chemical composition, mass concentrations and number size distribution in three cities of Western Europe: Milan, Barcelona and London. The objective are: 1) to provide a comprehensive picture on the involvement of the above cited microphysical processes in the regular daily, weekly and seasonal evolution of the urban aerosol, and 2) to

study the microphysical processes leading to high mass concentration episodes by linking the aerosol chemistry with the changes in the number size distribution. For this purpose, the data set from each study city was analysed in detail. Because the size of the data base and because we have made an effort in avoiding strong data reductions (e.g. avoiding so many "averages" which lead to information looses), the set of analysis performed provided a large amount of results. We have made an effort for synthesizing in one single article the key findings, in order to provide this general view of fine urban aerosols. Finally, the implications of these findings on our current "view" of urban aerosol pollution are discussed.

2 Study regions

The factors affecting the pollutants transport and dispersion, as well as the aerosol composition, in Western Europe experience significant variations from South to North (Millán et al., 2002; Rodríguez et al., 2007). The three cities selected for this study are representative of some of these differences (Fig. 1).

London is located within a meteorological context favouring the frequent renovation of air masses. This is due to the relatively flat terrain, the predominant mean westerly winds and frequent passages of cold fronts and depressions resulting in rain (Fig. 1). These are the predominant conditions at the North of the Alps and Pyrenees. In contrast, the areas surrounding the Western Mediterranean basin are characterised by an abrupt topography, which coupled with the characteristic synoptic scale patterns, results in low mean wind speeds and regional circulations that hinder the air mass renovations and favour the accumulation of aerosols in the surrounds of the emission regions (Fig. 1).

Barcelona is within a region where meteorological conditions favour the occurrence of high background levels of PM due to: 1) the predominant meteorology favouring regional pollution events because of weak gradient conditions and regional recirculations, 2) the low precipitation rates in the region (the lowest of Europe) which enhances

the residence time of aerosol, 3) an enhancement of the mineral dust resuspension processes in cities (by road traffic) due to the scarce roads cleaning because of the low precipitation rates, and in rural areas due to the arid soils.

Milan is within the bottom of the Po valley, where intense urban pollution events are favoured by the very low wind speed and the frequent occurrence of inversion layers near the ground in winter.

These differentiated conditions in the three cities are clearly evidenced in the local meteorological variables, such as in-situ wind speed (Fig. 1f) and the boundary layer depth (BLD; Fig. 1e). For example, observe how in summer the BLD maximises in Milan and London because of the thermal convective activity, whereas in Barcelona it exhibits a minimum owing to the subsidence over the coast because of the vertical recirculation of air masses along the coastal ranges (resulting in a decrease in the "thickness of the in-land sea breeze layer").

Another factor that contributes to differentiate the Mediterranean aerosol composition is the Saharan dust transport, which occurs with a much higher frequency in Southern than in Central-Northern Europe.

3 Methodology

This study was performed in central urban background sites of Milan (Via-Messina), Barcelona (Institute "Jaume Almera" – CSIC) and London (Bloomsbury).

3.1 Aerosol chemical characterization

Sampling of PM2.5 (24-h sampling) was performed on quartz filters once every 4 days using DIGITEL™ high volume samplers. After filter conditioning, mass concentrations were determined by gravimetry. The concentrations of non-sea-salt-$SO_4^=$, NO_3^-, NH_4^+, sea salt (Na+Cl+sea-salt-$SO_4^=$), mineral dust (Al_2O_3+SiO_2+Ca+$CO_3^=$+Ti+Fe+Sr), organic matter (OM=1.6*OC) and black carbon (BC) and some trace elements, were de-

termined by ion chromatography, thermal-optical-reflectance, ICP-AES, ICP-MS and some indirect determinations described by Querol et al. (2001) and Cao et al. (2004). A total of 96, 94 and 65 PM2.5 samples from Milan, Barcelona and London were analysed in this 1-year study, respectively.

3.2 Aerosol physical characterization

Aerosol number size distribution measurements were performed by using TSI™ Differential Mobility Particle Sizers (particle size 10-800nm in MILAN and BARCELONA and 10–415 nm in London).

Gravimetric equivalent hourly mass concentrations of PM2.5 were determined by multiplying the hourly concentrations of aerosol volume (in Milan), "GRIMM™" PM2.5 (in Barcelona) and "TEOM™" PM2.5 (in London) by factors (slope of the linear relationships) obtained by cross correlating the PM2.5 concentrations determined by the filter sampling versus the aerosol volume (Milan), the "GRIMM™" PM2.5 (in Barcelona) and the "TEOM™" PM2.5 (in London), respectively.

At Milan and Barcelona, these measurements were performed from November 2003 to December 2004. At London, the number size distribution was measured from January to December 2003, whereas the chemical characterization was performed from April 2004 to April 2005.

4 Results and discussion

The results are presented in several specific sections which gives response to the main questions which prompted this study. Because during the data treatment we tried to avoid strong data reductions, some of the figures that will be shown in the following sections provide a high density of information. Our discussion will focus only on the most relevant points and mainly in the common aerosol features at the three sites.

4.1 Mean physical properties

Table 1 and Fig. 2 show the mean PM2.5 and number concentrations, as well as the mean size distributions at the three study sites. Annual mean concentrations of PM2.5, N>10(nm) and N10-100 at the three sites are within the range of typical values across Western Europe (Ruuskanen et al., 2001; Van Dingenen et al., 2004), PM2.5: 20–45 $\mu g/m^3$, N>10(nm): 10–25$\times 10^3$ cm^{-3} and N10-100: 10–20$\times 10^3$ cm^{-3}. N10-415 accounts for ~99% of N>10(nm), whereas the ultrafine fraction N10-100 accounts for 80–85% of N>10(nm) at the 3 sites. The Milan and Barcelona to London ratios for PM2.5, N>10(nm) and N10-100 are equals to 2.3, 2.2 and 2.3 and 1.3, 1.5 and 1.5, respectively. The mode of the number (DpN: ~37nm), surface (DpS: 180–230 nm) and volume (DpV: 300–440 nm) size distribution exhibits the very well known displacement toward coarser fractions.

4.2 Mean chemical composition

Table 2 shows the mean chemical composition of PM2.5. The 'most to less' important PM2.5 contributors are: 1) OM (28–31% of PM2.5), 2) NO_3^- at Milan (21%) & London (11%) and nss-$SO_4^=$ at Barcelona (14%), 3) nss-$SO_4^=$ at Milan (10%) and London (9%) and NO_3^- at Barcelona (10%), 4) NH_4^+ (10% at Milan and 6–7% at Barcelona and London), and 5) BC (6–7%). Mineral dust concentrations are much higher at Barcelona (4.6 $\mu g/m^3$) than at the other sites (1.7 $\mu g/m^3$ at Milan and 0.6 $\mu g/m^3$ at London), whereas nss-$SO_4^=$ concentrations are much lower in London (2.8 $\mu g/m^3$) than in the other sites (4.6 $\mu g/m^3$).

MILAN exhibits the highest PM2.5 concentrations because of the much higher concentrations of OM and ammonium-nitrate. The difference PM2.5 (Milan) minus PM2.5 (Barcelona or London): 15 μgPM2.5/m^3 = 7.0 $\mu g NO_3^-/m^3$ + 5.5 μgOM/m^3 + 2.5 $\mu g NH_4^+/m^3$.

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4.3 Aerosol daily evolution

The processes prompting the daily evolution of aerosols have been studied by performing the following analysis: 1) the daily evolution of the hourly mean values of the "road traffic intensity", "primary trace gases concentrations (CO, NO_x and SO_2)" and "several aerosols parameters (including the size distribution mode, mass concentrations and number concentration in several size ranges)" during every day of the week (Fig. 3), 2) calculation of the increase ratio in the aerosol concentrations from the "nocturnal background (02:00-05:00)" to the "morning rush hours (06:00–08:00)" and to the whole "daylight period (06:00–18:00)" for the mass concentrations and for the number concentrations in several size ranges (Fig. 4), 3) calculation of the correlation coefficient between the weekly evolution of the aerosol mass concentrations, aerosol number concentrations (in several size ranges) and trace gases linked to combustions emissions (Fig. 5). The following discussion is based on the results plotted in Figs. 3–5.

All metrics of the aerosol concentration exhibit a maximum during the morning rush hours of the working days owing to the vehicles emissions (Figs. 3a–b). Road traffic emissions result in a higher increase in the concentrations of ultrafine (<100 nm) than in the coarser particles (Fig. 4). The "morning-rush hours" to "nocturnal-background" concentrations ratio is 1.5–3.0 for particles <50 nm and ≤1.5 for particles >200 nm (Fig. 4a1). The same trend is observed for the increase from the 'nocturnal-background' to the whole "daylight period" (Fig. 4b1). The DpN particle diameter (dN/dlogD mode) exhibits values within the ranges 35–50 nm during daylight and 50–70 nm at night (Fig. 3c). This daily evolution is the result of: 1) an abrupt DpN decrease in the morning because the sharp increase in road traffic emissions, 2) low DpN values along the daylight owing to the "contribution of photochemical nucleation particles", "evaporation of semi-volatile compounds from the particle's surface" and the still on course vehicle emissions (with a lower intensity than in the morning), and 3) a strong nocturnal DpN increase owing to the lack of significant emissions and the particles growth because the effects "particles coagulation" and "condensation of

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semi-volatile species onto pre-existing particles". The daylight-to-night change in the ambient conditions influences on this DpN daily evolution, by favouring evaporation during daylight (due to the increase in temperature and to the decrease of the gas-phase precursors concentrations owing to the dilution induced by the higher boundary layer depth; Fig. 1e) and condensation at night (conditions opposites to the diurnal ones). Particle growth by coagulation in short time scales (~hours) is the origin of the low residence time of particles <50 nm that we have observed, and contributes to the above cited high "morning-rush hours" and "daylight" to "nocturnal-background" concentrations ratios (Fig. 4). Notice how N10-20 experiences a strong decrease after the evening-rush hour, which is not observed in the number concentration of particles >100 nm owing to: 1) the growth of particles with an initial size <100nm contributes to N>100(nm), and 2) coagulation is not as important for particles >100 nm. These observations on the road traffic influence on the aerosol number size distribution, its daily evolution and the working-days to weekends changes, agrees with other observations in urban areas (e.g. Wehner et al., 2002; Wehner and Widensohler, 2003; Kittelson et al., 2004; Harrison and Jones, 2005).

This analysis of the urban aerosol in the 3 study cites shows that:

1) the ultrafine particles N10-100 better reflect road traffic emissions than PM2.5 (e.g. observed this at MILAN in Fig. 3a1–b1). This is also valid for N>10(nm) owing to the ultrafine fraction N10-100 accounts for a very high portion of N>10(nm) (80–85%).

2) the daily evolution of PM2.5 is much better correlated with that of N>100(nm) than with that of dominant ultrafine N10-100 particles (Fig. 5). Observe in Fig. 3 how the above description for the particles >100 nm applies for PM2.5 as well. This is attributed to the fact that particles >100nm contributes to the aerosol mass and volume much more than ultrafine particles (even the later accounts for 80–85% of the total number of fine particles; Fig. 1).

3) the daily evolution of the road traffic derived gas pollutants correlates better with the number concentration N than with PM2.5 (Figs. 5a2–d2).

4.4 Seasonal evolution and PM2.5 events

Figure 6 shows the "daily mean concentrations of PM2.5 including its most important contributors", and the "hourly mean values of the aerosol size distribution mode (DpN), aerosol mass PM2.5 concentrations and aerosol number concentration in several size ranges'. In order to identify the processes involved in the "day-to-day changes of the aerosol features" and in the "seasonal evolution of aerosols", the following analysis were applied to the data plotted in Fig. 6: 1) the occurrence of "urban PM pollution episodes", "African dust outbreaks" and "clean air events" was identified on the basis of the meteorology by analysing the time series of several aerosol parameters (using a methodology described in Rodríguez et al. (2005, and references therein); see some examples in Fig. 7), and 2) a study of the mean chemical composition and daily evolution of aerosols during events of low (PM2.5<30th-percentile), mid (30th<PM2.5<80th) and high (PM2.5>80th) mass PM2.5 concentrations (Fig. 8).

Some of the PM2.5 chemical components exhibit features commonly observed across Europe (Fig. 6): 1) BC, OM and NO_3^- levels maximises in winter, 2) nss-$SO_4^=$ exhibits higher background levels and a higher relative contribution in summer, and 3) nss-$SO_4^=$ and NO_3^- mainly occurs as ammonium salts (ionic balance analysis not shown). Moreover, the number concentration in all size ranges exhibits higher levels in winter than in summer (Fig. 6). This winter maximum is prompted by several mechanisms, such as: 1) concentration of PM and its gaseous precursors owing to the less "dilution" prompted by the "lower boundary layer depth", and 2) lower temperature that favour condensation and rapid nucleation from fresh emissions. The differences in the aerosol mean concentration and in the intensity of the winter maximum observed at the three studied cities are strongly related to the meteorological features described above (Fig. 1).

As stated above, the occurrence of the main types of "aerosol episodes" was identified on the basis of the meteorology (details on meteorological features will not be discussed here). As expected, "low PM – clean air episodes" mostly occurred dur-

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ing high wind speed events (frequently associated with air masses renovation linked to cold front passages), "PM pollution episodes" were favoured by weak baric gradient conditions and anticyclonic situations (frequently associated with winter inversion layers near the ground at MILAN), and "Saharan dust transport" occurred under well known meteorological scenarios.

The most important PM2.5 pollution events occur in winter, when OM and ammonium-nitrate are the most important contributors (these components accounts for 75%, 50% and 47% of PM2.5 mass in winter (November–February) and 32%, 25% and 34% of PM2.5 in summer (June–August) at Milan, Barcelona and London, respectively). During periods dominated by concatenations of "urban pollution events" and "clean air-low PM episodes", the daily mean PM2.5 and DpN time series show significant correlations, indicating that PM2.5 is made up of coarser particles during "pollution events" than under "clean air conditions". Figure 7 (where the types of events are highlighted) shows some examples from the three studied cities, where it can be observed how DpN increases from 30 to ~65 nm are associated with PM2.5 increases from 20 to 80 μg/m^3 at Milan and Barcelona and to 50 μg/m^3 at London, from "clean air" to "urban pollution" events. Observe in Fig. 8 (where the mean chemical composition and daily evolution of aerosols under different pollution degrees is shown) how the increase in the aerosol PM2.5 mass concentrations throughout the sequence "low-mid-high" levels is associated with an increase in the nocturnal DpN values, leaving the diurnal DpN values relatively constant throughout the sequence. This indicates that an increase in the aerosol PM2.5 mass concentrations is associated with an enhancement in the nocturnal particle growth described above ("daily evolution" section). A detailed event-to-event analysis corroborates this simultaneous DpN and PM2.5 correlated increases at night during PM2.5 episodes (examples of episodes not shown for the sake of brevity).

Although both "coagulation between particles" and "condensation of semi-volatile species onto pre-existing particles" may contribute to this nocturnal particle growth just described above (Figs. 8a to c), only condensation may accounts for the observed

simultaneous increase in the particle's DpN diameter and mass PM2.5 concentrations. This condensation of semi-volatile species is enhanced when temperature decreases (e.g. winter vs. summer or night vs. daylight) and when reducing the "boundary layer depth" (owing to less dilution increases the concentration of gas-phase precursors favouring that these compounds easily exceed the equilibrium vapour pressure, i.e. supersaturation). Our data points that condensation onto pre-existing particles of ammonium-nitrate at the three study sites and some OM species at MILAN are strongly involved in the particle growth from the "mid" to "high" PM2.5 events (when the highest "daylight-to-night" DpN increase is observed; Fig. 8c). This is supported by these observations (Fig. 8):

1) ammonium and nitrate are the compounds exhibiting the highest increase from "mid" to "high" PM2.5 episodes at the three sites, with "high/mid concentration" ratios= 4.5 and 2.9 at Milan and London, and =3.5 and 2.5 at Barcelona for nitrate and ammonium, respectively, and <2 for the other major components (except for OM at Milan). This nocturnal formation of ammonium-nitrate, that would increase the particle diameter by condensation, has already been documented (Weber et al., 2001 and Alastuey et al., 2004).

2) the increase in the concentrations of OM from "mid" to "high" PM2.5 episodes is much higher than that of BC at Milan ("high/mid" events ratios= 3.1 for OM and 1.5 for BC) than at Barcelona (1.5 for OM and 1.2 for BC) and London (1.4 for OM and 1.1 for BC). Because the BC (a primary particle) increase is mainly attributed to the lower dilution during pollution episodes (because the lower "boundary layer depth"), the much higher OM increase at Milan is attributed to condensation processes (secondary OM formation).

These enhanced condensation conditions at Milan with respect to the other sites, are favoured by: 1) lower winter temperatures, and 2) the much lower boundary layer depth due to the frequent occurrences of winter temperature inversions layers. This enhanced condensation may accounts for the: 1) larger summer-to-winter increase in OM, DpN and N>100(nm) at MILAN than the other sites (see these ratios in the up-

per left corner of Figs. 6c, 6g, 6j), 2) much higher winter (~9.5) than summer (~5.8) OM/BC ratios at Milan, whereas these ratios remains relatively constant from summer to winter both at Barcelona (~5.2) and London (~5.6). Notice how the most important daylight to night DpN increase is observed in Milan (Fig. 8), where the highest concentrations of semi-volatile components (ammonium-nitrate and unidentified OM species) are recorded.

Saharan dust transport also contributed to PM2.5 levels (Fig. 6d): 4 events occurred in Barcelona (over 94 filter samples), 3 events in Milan (96 samples) and any one in London (65 samples). Mineral dust concentrations during these Saharan dust episodes were into the ranges 8–15 $\mu g/m^3$ in Barcelona and 4–11 $\mu g/m^3$ in Milan. During mineral dust events attributed to local urban sources (e.g. road traffic resuspension, demolition and contribution works), dust concentrations within the ranges 7–22 $\mu g/m^3$, 3–6 $\mu g/m^3$ and 1–2 $\mu g/m^3$ in Barcelona, Milan and London, respectively, were observed. Mineral dust experiences a seasonal evolution with a winter maximum both at Milan and London, and a summer maximum in Barcelona.

Finally, in the examples shown in Fig. 7, it can be observed how the total number concentration N>10(nm) also tend to increase from the "clean air" to the "urban pollution" events, frequently from $<1\times10^4$ to $>2\times10^4\,cm^{-3}$. However, the degree of correlation between PM2.5 and the number concentration changes significantly depending on the particle size. Observe, in the examples shown in Fig. 7, how: 1) N>100(nm) shows a good correlation with PM2.5, 2) N10-100 may exhibit concentrations equally high during both high and low PM2.5 concentrations episodes, 3) N10-30 may even reach higher concentrations during low than during high PM2.5, and 4) the number concentration and DpN doesn't experience any significant variation during the Saharan dust events. These relationships are "quantified", and its origin discussed, in the following section.

4.5 Relationship between PM2.5 and number size distribution

The relationship between the aerosol PM2.5 mass concentrations and the number size distribution has been studied by: 1) calculating and analysing the correlation coefficient between PM2.5 and the number concentration in several size ranges (Fig. 9), 2) analysing the "scatter plots" of PM2.5 versus the number concentration in several size ranges (Fig. 10), and 3) calculating and analysing the correlation coefficient between the main PM2.5 chemical constituents and the number concentration in several size ranges (Fig. 11). The following discussion is based on these analysis performed over the 1 year data base.

Because the particle mass increases with the particle size, the correlation between PM2.5 and number concentrations increases with the particle diameter, from "r"<0.2 for 10–20 nm to 0.6–1.0 for >400 nm (Fig. 9a). As consequence, PM2.5 correlates much better with N>100(nm) (a fraction which only accounts for a 15–20% of the total number concentration N>10(nm)) than with the dominant ultrafine fraction N10-100 (Fig. 9).

The correlation of most of PM2.5 components with the number concentration increases with the particle diameter (Figs. 11c–k, this analysis is not available for London). This is more clearly observed for secondary species such as nss-$SO_4^=$, NO_3^- and NH_4^+ (Figs. 11f, g and h), whose gas-to-particle conversion rates onto the surface of pre-exiting particles are favoured under the presence of particles with a large surface (such as those >100nm; Fig. 2b): "according to the Kelvin effect the equilibrium vapour pressure over a sphere increases when the sphere's diameter decreases". In contrast, BC and OM exhibits high "r" values both in the ultrafine and >100 nm size fraction owing to the primary vehicles emissions and the subsequent particle growth by coagulation and condensation (Figs. 1d–e). Observe how BC and OM are the only components exhibiting a significant correlation with the ultrafine N10-100 particles (Figs. 11a–b). These size distributions of the correlation coefficients (Figs. c–k) resemble those of the chemical PM2.5 components obtained by cascade impactor sampling (Putaud et al.,

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2004; Cabadas et al., 2004).

Because both the particle's surface and mass increases with the particle's diameter, the N>100(nm) number, mass PM2.5 concentration and surface concentrations are positively correlated (Figs. 9, 10c–d). This indicates that: 1) an increase in N>100(nm) results in an increase of the aerosol surface available for gas-to-particle transfer of matter by condensation, and 2) "urban PM2.5 pollution events" mostly occurs when particles are grown enough to result in high N>100(nm) values (e.g. by condensation onto the surface of pre-existing particles of ammonium-nitrate; Figs. 11f–h). Observe in Fig. 7 how N>100(nm) is the only particle's size fraction that exhibits high concentrations only during PM2.5 episodes.

4.6 PM2.5 versus ultrafine particles events

The data analysis described above (Figs. 7–11) also allowed to study the relationship between aerosol PM2.5 mass and ultrafine N10-100 particles events.

The relationship of the ultrafine N10-100 fraction (and its subsets) with PM2.5 is more complex than the "simple positive correlation between PM2.5 and N>100(nm)". Observe in Fig. 7 how N10-30, N10-100 and N>10(nm) may exhibits high concentrations during both high and low PM2.5 events. According to the involvement of the different microphysical processes on the relationship between PM2.5 and ultrafine particles, we distinguish these events:

A) Simultaneous high or low "PM2.5 and N10-100 events" are observed during concatenations of some "clean air" and "PM2.5 pollution" events (e.g. 1–7 and 29–31 March 2004 at Milan, 1–9 February 2004 at Barcelona or 1–12 November 2003 at London; Fig. 7), when the previously discussed influence of meteorology results in the increase or decrease of PM concentrations. The data of the central part of the PM2.5 vs. N10-30 and PM2.5 vs. N10-100 scatter plots are associated with this type of events (Figs. 10a–b). During these episodes, the increase in PM2.5 levels occur because particles have grown enough to produce a significant N>100(nm) values (observe in Fig. 7 the DpN and N>100(nm) increases during the above cited examples).

B) Low PM2.5 and high N10-100 episodes (also associated with N10-30 events) are frequently recorded (e.g. 20–24 of March 2004 at Milan, 9–13 and 17 of February 2004 at Barcelona and 21–22 and 24 of November 2003 at London; Fig. 7). These events are caused by the occurrence of "very small fresh particles" (observe in Fig. 7 the low "DpN and N>100(nm)" and high "N10-30" values during the above cited examples) associated with two possible processes: 1) recent primary emissions (e.g. BC and some OM species) and 2) new particles formation by nucleation (e.g. sulphate and some OM species; Jung et al., 2006). The fact that the aerosol surface concentrations are low during these events (Fig. 10d) favours the occurrence of these very small particles, because under low aerosol surface concentrations: 1) the coagulation rates remain low (increasing the residence time of these fresh small particles), and 2) the condensation rates decreases and consequently the gas-to-particle transfer of matter by nucleation is favoured with respect to higher PM2.5 concentration events (this is due to the fact that condensation and nucleation are competing processes, being the first favoured under high aerosol surface concentrations and vice versa; see a discussion on this in Rodríguez et al., 2005). This type of events accounts for the data located in the right lower corner ("labelled as fresh PM") of the PM2.5 vs. N10-30 and PM2.5 vs. N10-100 scatter plots (Figs. 10a–b).

C) High PM2.5 and low N10-100 episodes. Examples (Fig. 7): 4 and 13–15 March 2004 at Milan and 7, 18–19 and 21 February 2004 at Barcelona. The following mechanisms may be involved in these events: 1) an enhancement of coagulation and condensation processes in relatively "aged air" (e.g. during pollution events at night; Fig. 8c), and 2) the presence of high density primary particles (e.g. fly-ashes, metals or mineral local or Saharan dust). These types of events account for the data located in the left upper corner ("labelled as aged PM" according to the first mechanism cited above) of the PM2.5 vs. N10-30 and PM2.5 vs. N10-100 scatter plots (Fig. 10a–b).

The influence of the above cited mechanisms favouring the presence of ultrafine particles under low PM2.5 concentrations is also observed in Fig. 8: the decrease in the aerosol concentrations from "high-to-mid" and "mid-to-low" PM2.5 events exhibits

ratios ∼0.5 for PM2.5, 0.6 for N>100(nm), 0.8 for N10-100 and 0.9 for N10-30 at the 3 sites. Observe how the decrease is much less important for ultrafine particles. This could have implications for air quality improvements strategies: "a decrease in the aerosol precursor emissions may raise the ultrafine particles load in urban air". The relationships leading to these conclusions have also been observed in urban and rural areas (Wichmann et al., 2000; Laakso et al., 2003; Rodríguez et al., 2005).

5 Summary and conclusions

In this article, data on urban fine aerosol physicochemical characterization in Milan, Barcelona and London are studied. The analysis of the aerosol number size distribution, chemical composition and mass PM2.5 concentrations data, provides a comprehensive picture on the involvement of the different microphysical processes of the aerosol dynamics (i.e. nucleation, coagulation, condensation, evaporation, etc...) in the regular evolution of the urban aerosol in a daily, weekly and seasonal basis as well as in the aerosol evolution from clean to pollution episodes.

Mean concentrations of PM2.5 and N>10(nm) at the three sites are within the range of typical values across Western Europe, PM2.5: 20–45 $\mu g/m^3$ and N>10(nm): 10–25×10^3 cm^{-3}, being the highest concentrations recorded in Milan and the lowest in London. Ultrafine particles N10-100 accounts 80–85% of the total number concentration of fine aerosol, and the number size distribution mode (DpN) is ∼37 nm. The results of this study evidence the much higher levels of: 1) "mineral dust" in the Mediterranean cities (4.6 $\mu g/m^3$ in Barcelona, 1.7 $\mu g/m^3$ in Milan and 0.6 $\mu g/m^3$ in London) and 2) organic matter and ammonium-nitrate in the Po Valley (Milan 7.0 $\mu g NO_3^-/m^3$, 5.5 $\mu g OM/m^3$ and 2.5 $\mu g NH_4^+/m^3$ higher than in Barcelona and London). The links between "aerosol chemical composition and mass concentrations" with the "number size distribution" have been studied in terms of the involvement of the microphysical processes.

Because the particle's mass increases with the particle's diameter, the mass con-

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centrations of fine PM2.5 aerosols exhibits a high correlation with the number concentration of particles >100nm (N>100(nm) and its subsets) and a low correlation with the number of particles <100 nm (N<100(nm) and its subsets). These associations, which are consistently observed all across the analysis of the daily, weekly and seasonal evolution, as well as in the day-to-day aerosol variations, indicates that PM2.5 is significantly influenced by the microphysical processes leading to the presence of N>100(nm). The following positive correlations are observed: 1) ammonium-nitrate and ammonium-sulphate with N>100(nm), attributed to gas-to-particle transformation mechanisms involving "condensation onto" and/or "reaction with" the surface of pre-existing particles, 2) organic matter (OM) and black-carbon (BC) with both the ultrafine N<100(nm) and the coarser N>100(nm), attributed to road traffic emissions and subsequent particle growth due to coagulation and condensation processes. Moreover, OM and BC are the only aerosol components showing a significant correlation with the ultrafine particles, which is attributed to road traffic emissions.

The involvement of the different microphysical processes on aerosol variations in several time scales has been studied:

Daily evolution. Because the diurnal "primary emissions, nucleation and evaporation processes" and the nocturnal "particle growth by condensation and coagulation", aerosol tend to be lesser during daylight (DpN: 35–50 nm) than at night (DpN: 50–70 nm). Road traffic emissions results in a much higher increase in the ultrafine than in coarser particles: "nocturnal-background" to "morning rush hours" increase of 1.5–2.5 for ultrafine N10-100 particles and <1.5 for N>100(nm) and PM2.5.

Seasonal evolution and pollution PM2.5 events. Time series of daily mean values of DpN, PM2.5 and N>100(nm) tend to exhibits day-to-day correlated variations during the concatenation of "urban pollution events" and "classical clean air episodes (in terms of PM2.5)". This tendency to increase the DpN diameter when increasing PM2.5 concentrations is attributed to condensation of semi-volatile species, being ammonium-nitrate (and OM in MILAN) the component exhibiting the highest increase from "mid"-to-"high" PM2.5 episodes (when the highest DpN increase is observed). These results

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indicates that PM2.5 events tend to occur when condensation processes have made particles grown enough to produce significant concentrations of N>100(nm).

Ultrafine N10-100 versus PM2.5. Because the very low contribution of ultrafine N10-100 particles to the mass concentration of fine PM2.5 aerosols, N10-100 do not shows a systematic positive or negative correlation with PM2.5. N>100(nm) is the only particle size-fraction which exhibits high concentration only during PM2.5 episodes. Events of low PM2.5 and high N10-100 concentrations occur frequently, and these are attributed to fresh vehicles emissions and new particle formation by nucleation. These results have important implications on how aerosol pollution is being monitored, since most of observations are based in terms of mass concentrations (PM2.5). This study shows how PM2.5: 1) is mainly weighted by particles >100 nm, which only accounts for <20% of the total number concentration of fine particles, and 2) doesn't account for the dominant ultrafine N10-100 fraction of urban aerosols (>80% of fine particles). Because vehicles primary emissions mainly occur in the ultrafine fraction, a specific monitoring of the ultrafine aerosols is important.

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Table 1. Aerosol number (N) and mass (PM2.5) concentrations statistic at Milan (November 2003–December 2004), Barcelona (November 2003–December 2004) and London (April 2004–April 2005 for PM2.5 and January–December 2003). DpN, DpS, DpV: mode of the number, surface and volume size distribution. m1: mode of the mean size distribution, m2 and med.: mean and median of all hourly values of the size distribution modes. ND: number of daily mean data used for the calculations. [1]PM2.5: values calculated from sampling on filter (1day every 4-days), [2]PM2.5: values computed from continuous measurements after correcting for gravimetric equivalence.

	Milan			Barcelona			London		
N	cm^{-3}	%		cm^{-3}	%		cm^{-3}	%	
10–800	25833			16811					
10–415	25676	99		16759	99		11 409		
10–20	2455	10		1941	12		1348	12	
20–30	4145	16		3386	20		1986	17	
30–50	5634	22		3988	24		2693	24	
50–100	8365	32		5093	30		3302	29	
100–200	3795	15		1855	11		1601	14	
200–415	1283	5		496	3		475	4	
415–800	157	< 1		49	< 1				
nm	m1	m2	med	m1	m2	med	m1	m2	med
DpN	36	47	41	36	39	36	38	50	43
DpS	233	213	179	179	178	179	198	228	198
DpV	309	340	309	309	294	309	437	355	379
$\mu g/m^3$	ND	mean	90th	ND	mean	90th	ND	mean	90th
[1]PM2.5	96	47	87	94	34	55	63	31	45
[2]PM2.5	264	45	81	365	26	40	362	20	33

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Table 2. Statistic of PM2.5 composition based on 96, 94 and 65 samples collected in Milan, Barcelona and London from December 2003 to December 2004, December 2003 to December 2004, and April 2004 to April 2005, respectively. Trace elements: sum of Zn, V, Cr, Co, Ni, Cu, As, Cd and Pb.

	Milan			Barcelona			London		
	mean $\mu g/m^3$	%	90th $\mu g/m^3$	mean $\mu g/m^3$	%	90th $\mu g/m^3$	mean $\mu g/m^3$	%	90th $\mu g/m^3$
PM2.5	47.0		86.8	34.3		54.5	31.0		45.5
OM	14.8	31	32.3	9.7	28	14.8	9.0	29	14.3
BC	1.8	4	2.9	1.9	6	2.8	1.6	5	2.5
NO_3^-	10.1	21	23.4	3.5	10	8.0	3.5	11	9.3
nss-$SO_4^=$	4.6	10	8.4	4.6	14	9.1	2.8	9	5.5
NH_4^+	4.8	10	10.0	2.2	6	4.7	2.1	7	5.9
OM+BC	16.5	35	34.7	11.6	34	18.1	10.6	34	15.7
SIC	19.4	41	39	10.4	30	20	8.4	27	21.0
Mineral	1.7	4	3	3.7	11	8	0.6	2	0.9
Sea-salt	0.2	0.4	0.4	0.7	2.2	1	0.7	2.1	1.7
Trace	0.1	0.2	0.2	0.1	0.4	0	0.04	0.1	0.1
S chemistry	38			27			20		
%Determined	81			77			66		

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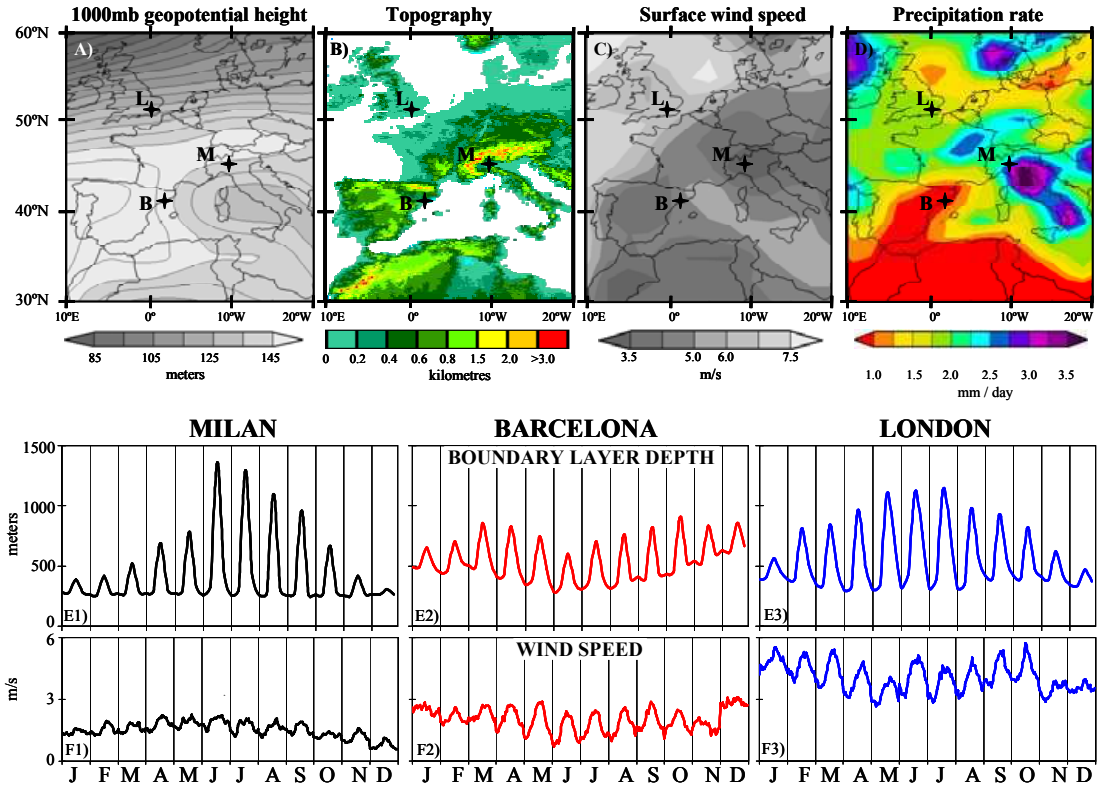

Fig. 1. Maps of topography and 2000–2005 climatology of several meteorological fields over Europe **(a–d)** and daily mean evolution per month during 2004 of the Boundary Layer Depth and in-situ wind speed **(e–f)** at London (L), Barcelona (B) and Milan (M).

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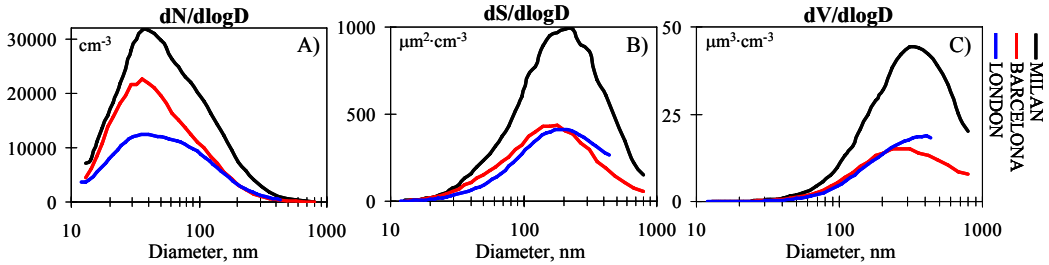

Fig. 2. Mean size distribution of aerosol number, surface and volume concentrations during the 1-year study period.

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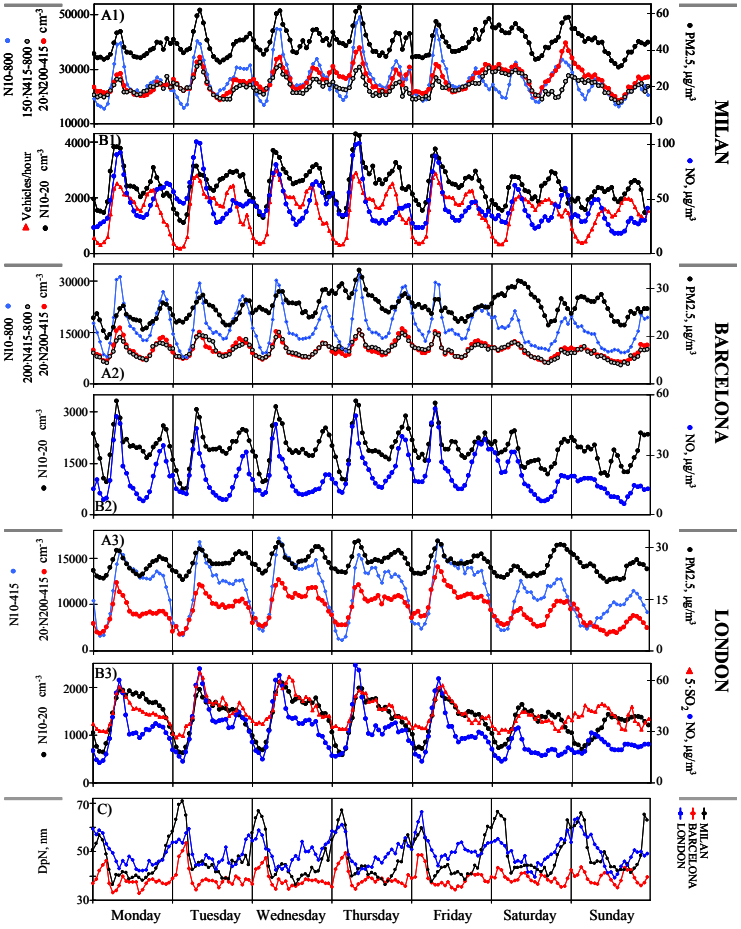

Fig. 3. Hourly mean concentrations of aerosol parameters, gaseous pollutants and road traffic intensity (only at MILAN) averaged over every day of the week during the 1-year study period.

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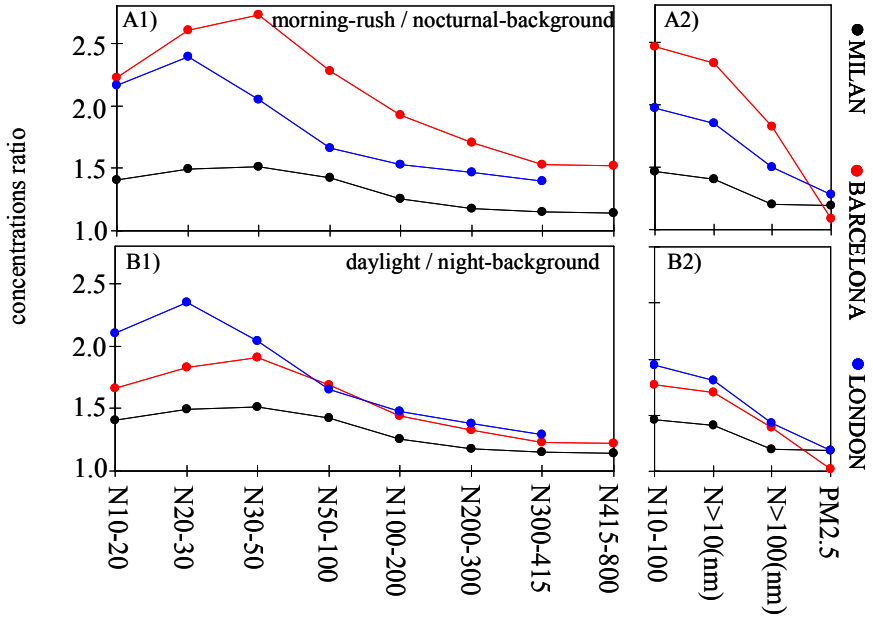

Fig. 4. "Morning rush hours (06:00–08:00) to nocturnal-background (02:00–05:00)" and "daylight (06:00–18:00) to night-background (02:00–05:00)" ratios of the aerosol PM2.5 mass and number concentration in several size ranges during working days of the 1-year study period.

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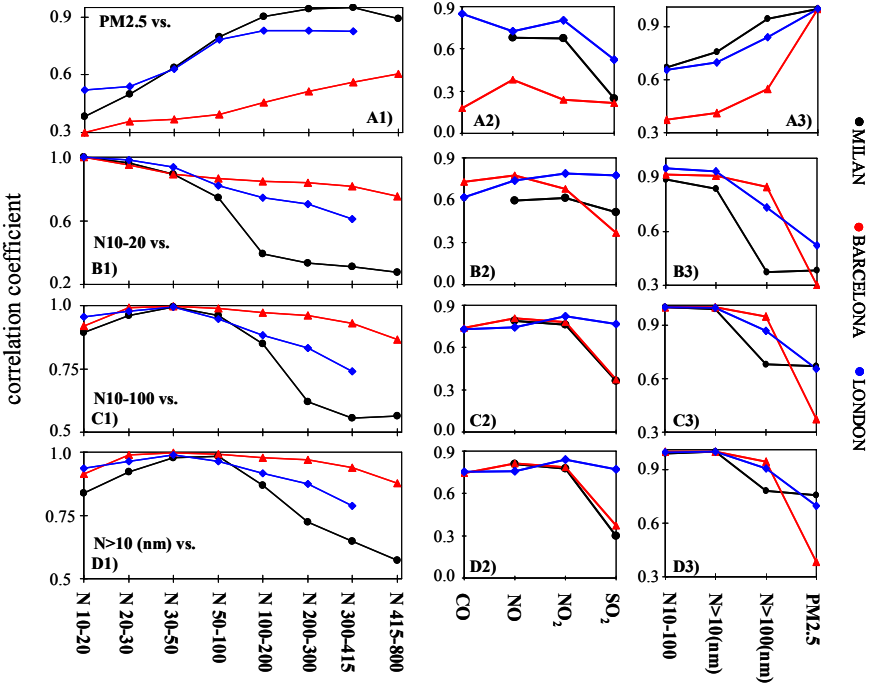

Fig. 5. Correlation coefficient between the weekly cycles (Monday to Sunday daily cycles) of "PM2.5, N10-20, N10-100 and N>10(nm)" and those of "the aerosol PM2.5 mass, number concentrations (in several size ranges) and gases".

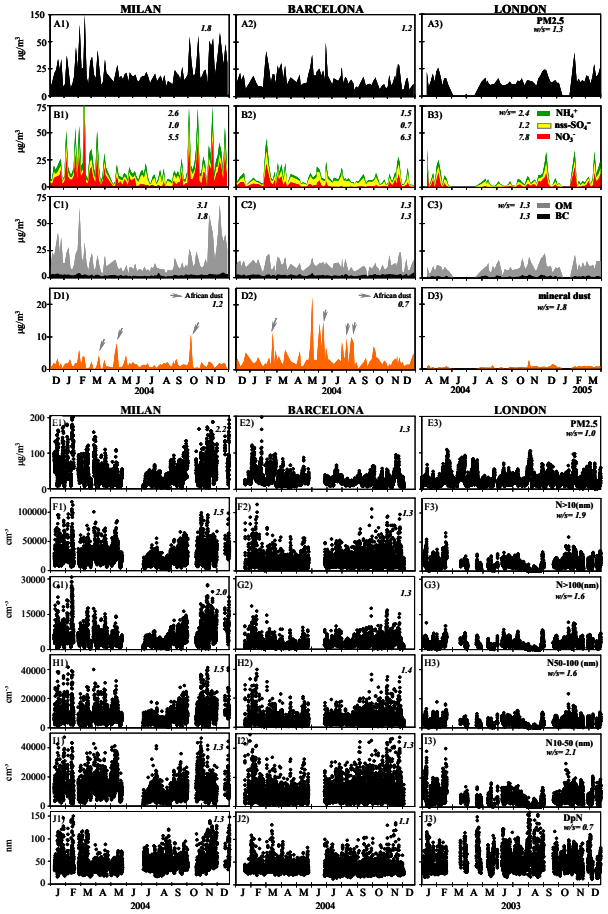

Fig. 6. Daily mean concentrations of PM2.5 and including its major contributors **(a–d)** and hourly mean concentrations of PM2.5 and the aerosol-number concentration in several size ranges **(e–j)**. w/s = mean winter (November–February)/summer (May–August) concentrations ratio.

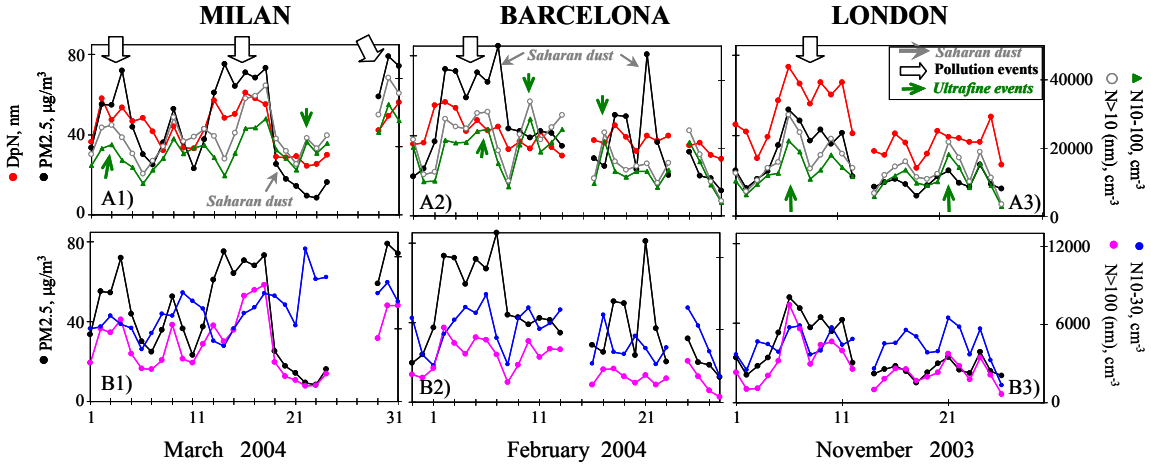

Fig. 7. Daily mean values of the aerosol PM2.5 mass concentrations, number concentrations (in several size ranges) and size distribution mode (DpN) at the 3 study cities during selected periods when different types of aerosol episodes took place. Events of "Saharan dust", "urban pollution" and "ultrafine particles" are highlighted (previous identification was performed by using the methodology described in Rodríguez et al. (2005, and references therein).

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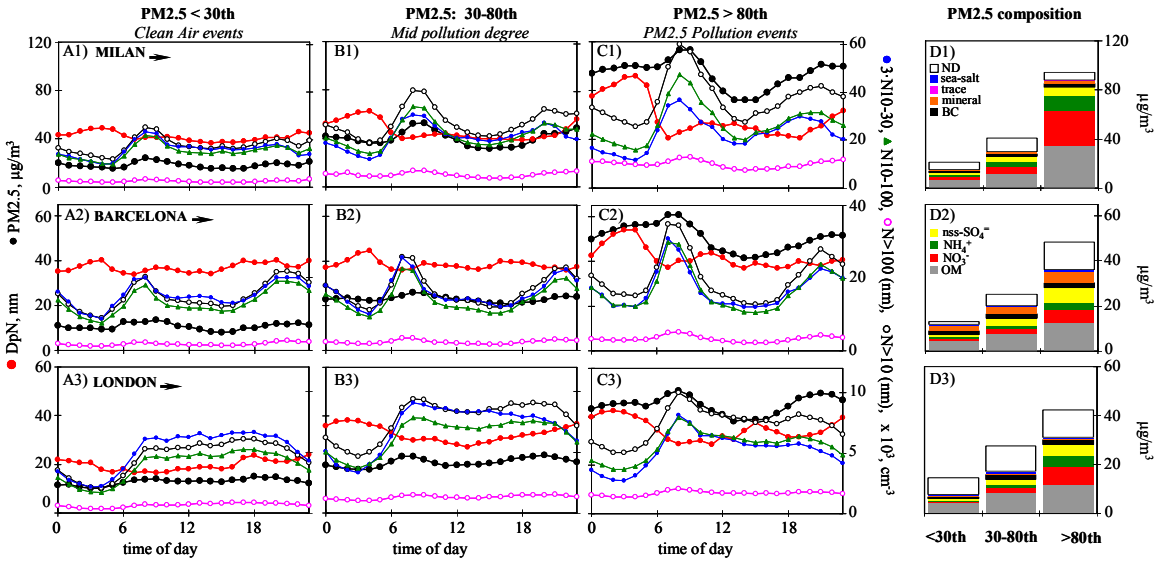

Fig. 8. Daily mean evolution of several aerosol parameters **(a–c)** and mean PM2.5 aerosol chemical composition during events of "low (<30th percentile)", "mid (30–80th percentile)" and "high (>80th percentile)' PM2.5 concentrations in the 3 study sites. **(d)**: "ND"=Non-Determined (PM2.5 – sum of chemistry), "trace" = trace elements (see Table 2), "mineral" = Mineral dust.

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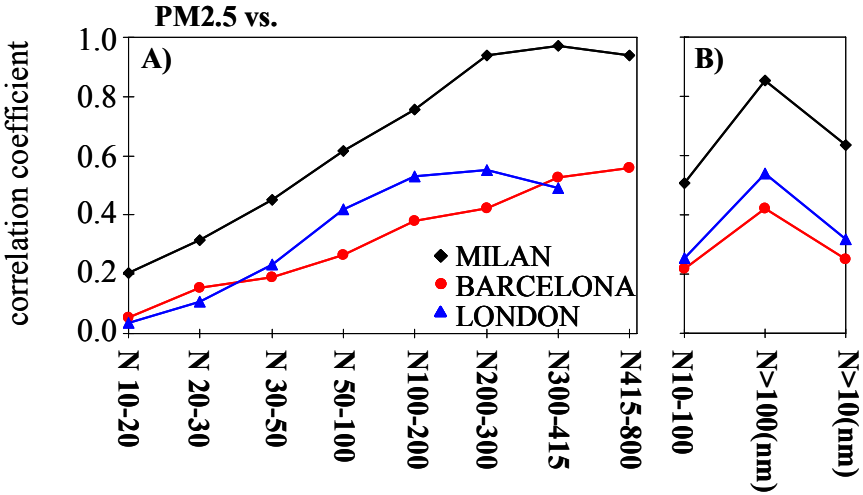

Fig. 9. Correlation coefficient between the aerosol hourly "mass PM2.5 concentrations" and "number concentration (in several size ranges)" during the 1-year study period (each value obtained with more than 8000 hourly data).

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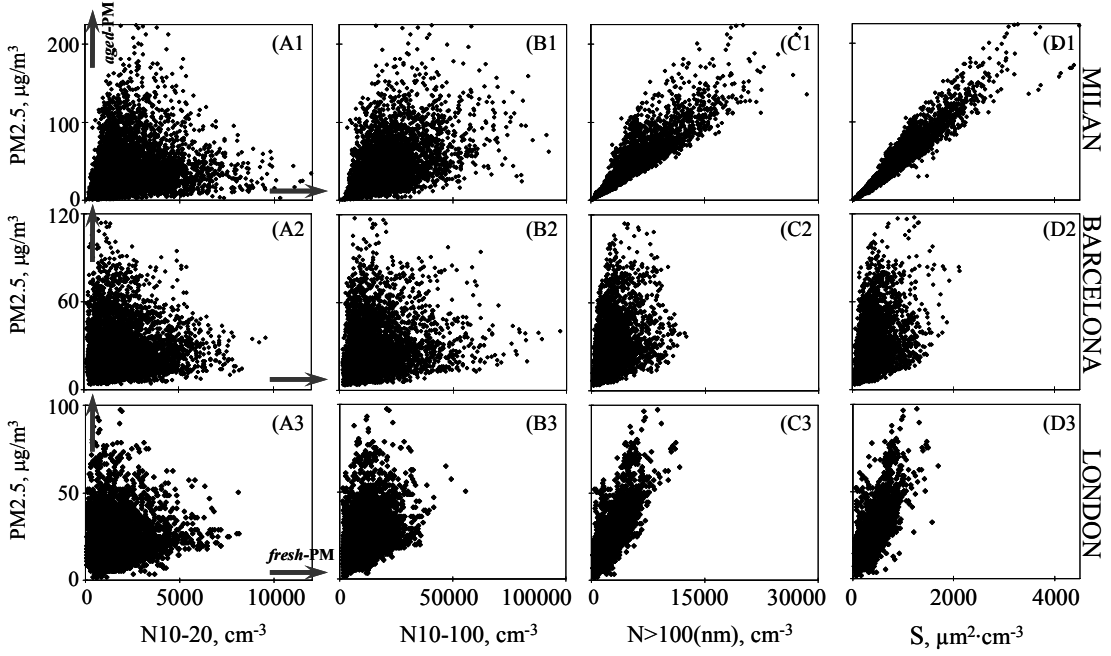

Fig. 10. Hourly mean aerosol PM2.5 mass concentrations versus number concentrations (in several size ranges) during the 1-year study period.

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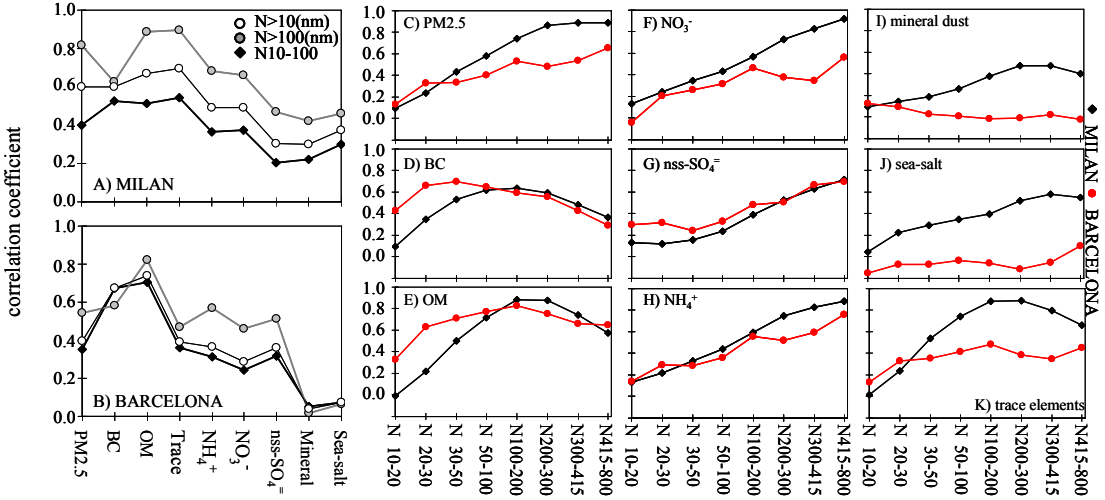

Fig. 11. Correlation coefficient between the daily mean aerosol PM2.5 mass concentrations and number concentrations (in several size ranges) during the 1-year study period.

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